Synthesis of Well-Defined, Functionalized Polymer Latex Particles through Semicontinuous Emulsion Polymerization Processes

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ABSTRACT: The design of a semicontinuous emulsion polymerization process, primarily based on theoretical calculations, has been carried out with the objective of achieving overall independent control over the latex particle size, the monodispersity in the particle size distribution, the homogeneous copolymer composition, the concentration of functional groups (e.g., carboxyl groups), and the glass-transition temperature with *n*-butyl methacrylate/*n*-butyl acrylate/methacrylic acid as a model system. The surfactant coverage on the latex particles is very important for maintaining a constant particle number throughout the feed process, and this results in the formation of monodisperse latex particles. A model has been set up to calculate the surfactant coverage from the monomer feed rate, surfactant feed rate, desired solid content, and particle size. This model also leads to an equation correlating the polymerization rate to the instantaneous conversion of the monomer or comonomer mixture. This equation can be used to determine the maximum polymerization rate, only below or at which monomer-starved conditions can be achieved. The maximum polymerization rate provides guidance for selecting the monomer feed rate in the semicontinuous emulsion polymerization process. The glass-transition temperature of the resulting carboxylated poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) copolymer can be adjusted through variations in the compositions of the copolymers with the linear Pochan equation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 30–41, 2003

Key words: emulsion polymerization; functionalization of polymers; modeling; calculations

INTRODUCTION

Functionalized (e.g., carboxylated) latex particles with well-defined characteristics, such as uniform particle sizes, homogeneous compositions, control over the functional group concentration and location within the particles, precisely controlled particle sizes, and adjustable glass-transition temperatures (T_g's), are of great importance in both academic research and industrial applications.[1–9] However, the preparation of these types of latex particles is challenging, especially when it is required that only one specific parameter changes (e.g., the concentration of functional groups) while the other properties remain constant.

Latexes can be synthesized by batch, semicontinuous (semibatch), or continuous processes. Of all the emulsion polymerization processes, the semicontinuous process offers many advantages, giving a formulator good control over the polymerization kinetics and copolymer composition through variations in the various reactant feed conditions. It is this versatility that has made the semicontinuous process the most widely used of all of the emulsion polymerization processes; for example, it is employed for the manufacture of coatings, binders, adhesives, and synthetic rubbers. Therefore, a carefully designed semicontinuous process would be a powerful method for synthesizing well-defined, functionalized latex particles.

The copolymerization of functional comonomers with the backbone (co)monomers that constitutes the bulk of the resulting copolymer is the most commonly used and convenient process for incorporating functional groups into latex particles.[10–18] The use of a semicontinuous process also offers advantages in controlling the location of the functional groups in the functionalized latex particles when these groups are incorporated with a copolymerization process. For example, when carboxyl groups are incorporated into a particle with methacrylic acid (MAA) as the functional comonomer, the carboxyl groups is distributed more uniformly throughout the particles with a semicontinuous process than with a batch polymerization process.[10,19–21] However, almost all of the studies describ-

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ing the preparation of functionalized latex particles with a semicontinuous process have been empirical in nature and have only allowed for the control of one experimental parameter at a time.[11–20] There is lack of well-designed semicontinuous processes that can control all of the aforementioned parameters simultaneously. Therefore, this article describes the development of a theoretical model that would be useful in designing semicontinuous processes with the objective of synthesizing well-defined, functionalized latex particles.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA), *n*-butyl acrylate (BA), and methacrylic acid (MAA) monomers (Sigma–Aldrich, Milwaukee, WI; reagent-grade) were purified by being passed through columns filled with an appropriate inhibitor-removal packing material (Sigma–Aldrich, Somerville, NJ). Sodium dodecyl sulfate (SDS; Fisher Scientific; reagent-grade) and potassium persulfate (KPS; Sigma–Aldrich; reagent-grade) were used as received without further purification. A cationic ion-exchange resin (20–50-mesh; AG 50W-X4, Bio-Rad Co., Hercules, CA) and an anionic ion-exchange resin (20–50-mesh; AG 1-X4, Bio-Rad) were cleaned with a method described in a previous publication.[22]

Latex synthesis

All syntheses were performed in a 500-mL, four-necked flask equipped with a reflux condenser, a nitrogen gas inlet tube, a poly(tetrafluoroethylene) stirrer (~230 rpm), and two feed tubes for monomer and surfactant solutions. The poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] copolymer latex was prepared by a conventional semicontinuous emulsion polymerization process at 80°C. Table I gives a typical recipe for the synthesis of the control noncarboxylated P(BMA/BA) latexes. For the synthesis of carboxylated P(BMA/BA) latexes, MAA was added to the monomer mixture (the weight fractions of MAA, BMA, and BA were adjusted according to the desired carboxyl group concentration and T_g), which was fed into the reactor (Table II). The initial 1.5-h period of the polymerization was the seeding stage. About 10% of the monomer mixture (BMA/BA = 75/25 w/w) was used in the seeding stage. After the seeds were almost fully formed (~95% conversion), the remaining monomer mixture of BMA, BA, and/or MAA (for carboxylated latex particles) and surfactant solution were separately fed into the reactor at constant rates with two syringe pumps (Harvard Apparatus 22, Hollistan, MA). When the feeds were finished, the reaction was allowed to continue for another 2 h, and the latex was then cooled to room temperature.

TABLE I
Typical Recipe for the Synthesis of P(BMA/BA) Copolymer Latex with a Semicontinuous Emulsion Polymerization Process at 80°C

Ingredient	Amount (g)
Seed stage	
BMA	26.25
BA	8.75
KPS	0.40 (3.29 m*M*)[a]
SDS	1.00 (7.72 m*M*)[a]
DI water	450.00
Feed stage	
Monomer mixture	
BMA	215.00
BA	71.70
Surfactant solution	
SDS	2.44
KPS	0.40
DI water	50.00

BMA:BA (w/w) = 3:1; the ratio can be adjusted according to the desired T_g; the monomer mixture and surfactant solution were fed separately at constant feed rates.

[a] Concentrations based on aqueous phase.

TABLE II
Recipe for the Synthesis of Carboxylated P(BMA/BA) Copolymer Latexes with a Semicontinuous Emulsion Polymerization Process at 80°C

Ingredient	Weight fraction	Amount (g)
Seed stage		
BMA	0.75[a]	26.25
BA	0.25[a]	8.75
KPS		0.40 (3.29 m*M*)[b]
SDS		1.00 (7.72 m*M*)[b]
DI water		450.00
Feed stage		
Monomer mixture		290.00
BMA	0.65–0.436[a]	
BA	0.339–0.497[a]	
MAA	0.0112–0.0668[c]	
Surfactant solution		
SDS		2.44
KPS		0.40
DI water		50.00

The monomer mixture and surfactant solution were fed separately at constant feed rates.

[a] Based on the monomer charged, which was adjusted to achieve a T_g of 0°C.

[b] Concentrations were based on the aqueous phase.

[c] Based on the monomer feed, adjusted according to the desired concentration of carboxyl groups and T_g.

Cleaning of latexes

The latexes were cleaned with an ion-exchange method before they were characterized.[22] This method uses analytical-grade anionic and cationic ion-ex-

change resins (Bio-Rad). The cationic ion-exchange resin was extensively washed with deionized (DI) water before use. The anionic ion-exchange resin was converted from its chloride form into its hydroxide form with a 3*N* aqueous sodium hydroxide solution and then was completely washed with DI water. The two cleaned resins were mixed in a weight ratio of 51:49 AG 50W-X4/AG 1-X8 just before use. Latex samples were diluted to approximately a 5% solids content. The ratio of the solid polymer to the mixed resins was 1:1, and the mixture was agitated with magnetic stirring or mechanical stirring for 2 h for each cleaning cycle. The conductance of the latex was measured after each ion-exchange cycle. This ion-exchange procedure was repeated until the conductance of the latex reached a constant value. This procedure usually required five cycles. Serum replacement cells were also used to preclean some of the latexes.[23]

Latex characterization

The particle size and particle size distribution were measured by capillary hydrodynamic fractionation (model 1100, Matec Applied Sciences, Northborough, MA). All the samples were sonified in a sonifier bath (Commonwealth Scientific, Alexandria, VA) to break up any latex particle aggregates before particle size measurements were carried out.

The surface carboxyl group densities were determined by conductometric titration with cleaned latex samples. The quantity of carboxyl groups in the aqueous phase was determined by the conductometric titration of the serum separated from the latexes by ultracentrifugation (L8-M ultracentrifuge, Beckman, Fullerton, CA; the conditions were 37,000 rpm, 4°C, and 12 h). The amount of the carboxyl groups buried within the latex particles was calculated by the subtraction of the carboxyl groups present on the latex particle surfaces and in the aqueous phase from the total carboxyl group content in a given recipe.

T_g's of the latex polymers were measured with differential scanning calorimetry (DSC; DSC 2920 scanning calorimeter, TA Instruments, New Castle, DE). Experiments were performed over a temperature range of −50 to 60°C or −60 to 250°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Well-defined, functionalized polymer latexes should meet the following requirements: (1) the particles should be uniform in size, (2) they should be available in various particle sizes, (3) the distribution of the functional groups should be controllable, (4) there should be independent control over the particle size and the density of the functional groups, (5) there should be independent control over T_g and the density of the functional groups, and (6) their composition should be homogeneous for copolymer latexes. Well-designed methods for preparing the particles are necessary to meet these requirements.

Strategy to control the monodispersity of the latex particle size

The process used to synthesize the well-defined, functionalized latex particles is seeded, semicontinuous emulsion polymerization. In this process, the key point needed to control the monodispersity of the latex particle size distribution is a constant particle number during the polymerization in the feed stage, which is determined by the seed number. This means that any secondary nucleation (resulting in an increase in the particle number) or any particle coagulation (resulting in a decrease in the particle number) has to be prevented. The maintenance of a constant particle number requires good control over the amount of the surfactant fed into the reactor during the semicontinuous process. It is necessary to calculate the surface coverage of the surfactant on the particles during the polymerization in the feeding stage to determine the appropriate amount of the surfactant that can maintain a constant particle number. The methodology to achieve this is given next.

Prediction of the surfactant coverage on the latex particle surfaces during polymerization during the feed stage

A theoretical calculation was initially used instead of an experiment to determine the surfactant coverage on the surfaces of the latex particles. The following model was used for this calculation. The assumptions used for this calculation are as follows: (1) monolayer adsorption of the surfactant occurs on the latex particle surfaces and (2) when the surfactant reaches 100% monolayer coverage on the particle surface, it reaches the critical micelle concentration (cmc; m*M*) in the aqueous phase simultaneously.

At any given feed time t (min), an equation can be established that is based on a mass balance:

$$R_m V_{a0} t c(t) + W_{m0} c(t_0) = \frac{1}{6} \pi D_v^3 \rho N_p V_{a0} \qquad (1)$$

where R_m is the feed rate for the monomer mixture in terms of the initial volume of the aqueous phase (g/min cm^3), $c(t)$ is the fractional instantaneous conversion (%), W_{m0} is the weight of the monomer used in the seed preparation step (g), $c(t_0)$ is the fractional conversion at the end of the seeding stage, D_v is the volume-average particle size (cm), ρ is the (co)polymer density (g/cm^3), V_{a0} is the initial volume (before feed) of the aqueous phase (cm^3), and N_p is the concentra-

tion of latex particles in terms of the initial volume of the aqueous phase at any given time t (number of particles/cm^3).

D_v can be determined by the rearrangement of eq. (1). The total particle surface area, S_p (cm^2), can be calculated from the particle diameter and total particle number. Substituting for D_v in eq. (3) from eq. (2) leads to a relation between S_p and the macroscopic parameters for semicontinuous polymerization :

$$D_v = \left(\frac{6}{\pi\rho N_p V_{a0}}\right)^{1/3} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{1/3} \quad (2)$$

$$S_p = \pi D_v^2 N_p V_{a0} \quad (3)$$

$$S_p = \frac{6^{2/3}\pi^{1/3} N_p^{1/3} V_{a0}^{1/3}}{\rho^{2/3}} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{2/3} \quad (4)$$

According to assumption 1, the surfactant weight needed to cover the entire surface area of the latex particles, W_{ssc} (g), is given by eq. (5), with monolayer surfactant coverage on the latex particles assumed:

$$S_p = \frac{W_{ssc}}{M_s} N_A a_s \quad (5)$$

where M_s is the molecular weight of the surfactant (g/mol), N_A is Avogadro's constant (molecules/mol), and a_s is the particle surface area occupied by each surfactant molecule at 100% surface coverage (cm^2/molecule).

An expression for W_{ssc} can be derived by the combination of eqs. (4) and (5):

$$W_{ssc} = \frac{6^{2/3}\pi^{1/3} N_p^{1/3} V_{a0}^{1/3} M_s}{N_A a_s \rho^{2/3}} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{2/3} \quad (6)$$

For monodisperse latex particles to be obtained from monodisperse seeds, the total particle number should be constant and equal to the seed particle number throughout the feed process:

$$N_p = N_{p0} = \frac{6 W_{m0} c(t_0)}{\pi D_{v0}^3 \rho V_{a0}} \quad (7)$$

where N_{p0} is the concentration of the latex particles in terms of the initial volume of the aqueous phase at the end of the seeding stage (number of particles/cm^3) and D_{v0} is the volume-average particle diameter at the end of the seeding stage (cm).

Substituting for N_p in eq. (6) from eq. (7) leads to eq. (8). The fractional surfactant coverage (σ_s) on the latex particles can be defined by eq. (9):

$$W_{ssc} = \frac{6 W_{m0}^{1/3} M_s c(t_0)^{1/3}}{N_A a_s D_{v0} \rho} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{2/3} \quad (8)$$

$$\sigma_s = \frac{W_{sad}}{W_{ssc}} = \frac{W_{stot} - W_{saq}}{W_{ssc}} \quad (9)$$

where W_{sad} is the weight of the surfactant adsorbed onto the latex particle surface (g), W_{stot} is the total weight of the surfactant used at any given feed time (g), and W_{saq} is the weight of the surfactant in the aqueous phase (g). W_{stot} and W_{saq} can be expressed as eqs. (10) and (11), respectively:

$$W_{stot} = R_s V_{a0} t + W_{stot0} \quad (10)$$

$$W_{saq} = [S]_{aq} M_s (1 + R_a t) V_{a0} \times 10^{-6} \quad (11)$$

where R_s is the feed rate of the surfactant in terms of the initial volume of the aqueous phase (g/min cm^3), R_a is the feed rate of deionized water in terms of the initial volume of the aqueous phase (g/min cm^3), W_{stot0} is the total weight of the surfactant used for the seeding stage, and $[S]_{aq}$ is the concentration of the surfactant in the aqueous phase (mM). Substituting for W_{ssc}, W_{stot}, and W_{saq} in eq. (9) from eqs. (7), (10), and (11) leads to eq. (12):

$$\sigma_s = \frac{N_A a_s D_{v0} \rho [R_s V_{a0} t + W_{stot0} - [S]_{aq} M_s V_{a0} (1 + R_a t)]}{6 W_{m0}^{1/3} M_s c(t_0)^{1/3} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{2/3}} \quad (12)$$

Three parameters (α, β, and d) are defined by eqs. (13)–(15):

$$\alpha = \frac{R_s}{R_m} \quad (13)$$

$$\beta = \frac{R_a}{R_m} \quad (14)$$

$$d = \frac{[S]_{aq}}{\sigma_s} \quad (15)$$

where α is the ratio of the surfactant feed rate to the monomer feed rate, β is the ratio of the aqueous phase feed rate to the monomer feed rate, and d is the distribution coefficient of the surfactant between the latex particle surface and the aqueous phase (mM).

Substituting for R_s, R_a, and $[S]_{aq}$ in eq. (12) from eqs. (13)–(15) and solving σ_s lead to eq. (16):

$$\sigma_s = \frac{\rho N_A a_s D_{v0} (\alpha R_m V_{a0} t + W_{stot0})}{6 W_{m0}^{1/3} M_s c(t_0)^{1/3} [R_m V_{a0} t c(t) + W_{m0} c(t_0)]^{2/3} + \rho N_A a_s D_{v0} M_s d V_{a0} (1 + \beta R_m t) \times 10^{-6}} \quad (16)$$

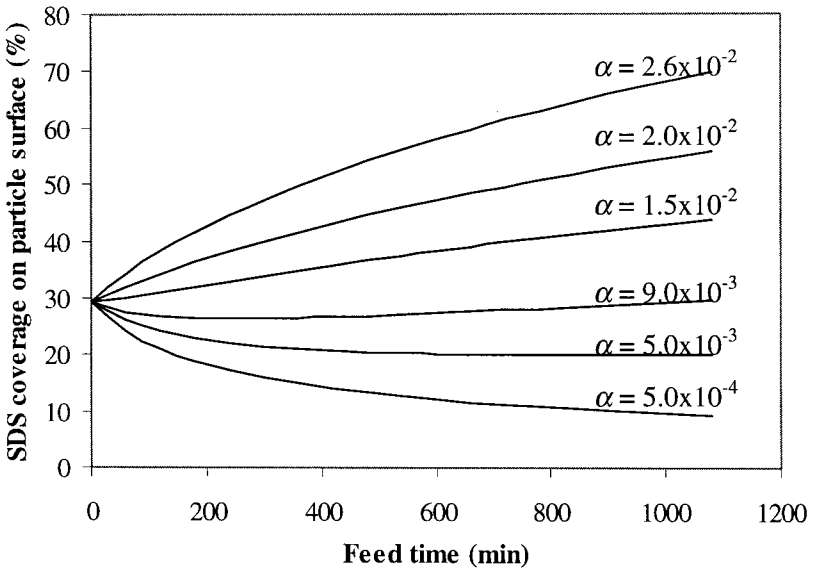

Figure 1 Surfactant coverage versus the feed time for different α values for the BMA/BA (65/35 w/w) copolymerization system stabilized by SDS (D_{v0} = 65 nm; β = 0.255; $R_m = 5.96 \times 10^{-4}$ g/min cm^3; V_{a0} = 450 cm^3; W_{m0} = 35 g).

In eq. (16), the variable is t, and the unknown initial parameters are α, β, d, and R_m. All the others quantities are constants or known initial parameters for the synthesis. If the feed rate of the surfactant is low as in a monomer-starved, semicontinuous emulsion polymerization process, the distribution of the surfactant between the latex particle surface and the aqueous phase is considered to be in equilibrium at any given feed time. Therefore, d could be assumed to be constant throughout the feed process. According to the definition of a_s, the surfactant coverage on the latex particles reaches 100% when the concentration of the surfactant in the aqueous phase reaches its cmc; the d value can be determined by the boundary condition ($d = [S]_{aq}/\sigma_s$ = cmc/1 = cmc), and it is found that the d value is equal to the value of the cmc. The parameter β is a variable that can be used to adjust the solid content, which is expressed by eq. (17), with a 100% monomer conversion being assumed and the weights of the surfactant and initiator being ignored:

$$\% \text{ Solids} = \frac{R_m V_{a0} t + W_{m0}}{R_m V_{a0} t + W_{m0} + V_{a0} + R_a V_{a0} t} \times 100\% = \frac{R_m V_{a0} t + W_{m0}}{(1 + \beta) R_m V_{a0} t + W_{m0} + V_{a0}} \times 100\% \quad (17)$$

Under given seed conditions (W_{m0}, V_{a0}, and D_{v0}) and with a desired particle size D_v, which is calculated with eq. (18), the only parameter that can be used to adjust the solids content is β:

$$D_v = D_{v0} \left(\frac{R_m V_{a0} t}{W_{m0}} + 1 \right)^{1/3} \quad (18)$$

Therefore, the parameter β can also be initially determined from the desired final solid content of the synthesized latex. Now, the remaining unknown initial parameters are α and R_m.

Determination of the surfactant feed rate able to maintain a constant particle number

For a given monomer or monomer mixture (ρ), surfactant (cmc, a_s, and M_s), and solids content (β) and given seed conditions (D_{v0}, W_{m0}, W_{stot0}, and P_0), σ_s is a function of t . Figure 1 shows plots of σ_s versus t at different α values for the BMA/BA copolymerization system stabilized by SDS at a given value of R_m (see Table I for the recipe used).

As shown in Figure 1, the profile of the surfactant coverage versus the feed time is determined from the α value. It was shown previously that at $\alpha = 2.0 \times 10^{-2}$, the particle number was kept constant throughout the semicontinuous emulsion polymerization.[10] In this article, the extreme α values, which could no longer maintain a constant particle number, were examined. When α was 0, the particles coagulated during polymerization. When α was 5.0×10^{-4}, the latex was stable, and the particle size was near the size predicted by eq. (18). However, these latexes were not stable during storage. If these latexes were not poststabilized with additional SDS, they coagulated in 1 day. Therefore, we can say that 5.0×10^{-4} is the minimum α value that can still maintain both a constant particle number during polymerization and latex stability. The upper limit of α was also examined. When α was greater than 2.6×10^{-2}, small particles could be observed with transmission electron micros-

copy, indicating that there was secondary nucleation. Therefore, the upper value of useful α is 2.6×10^{-2}. The safe range for maintaining a constant particle number for this specific system is $5.0 \times 10^{-4} < \alpha < 2.6 \times 10^{-2}$.

As long as the monomer feed rate is determined, the surfactant feed rate can be selected to fall within the aforementioned safe range. The α value that can maintain roughly constant surfactant coverage during the polymerization would be most preferred. A question now arises as to how one can determine the monomer feed rate; this issue is discussed in the following section.

Determination of the monomer feed rate

As discussed in the last section, the monomer feed rate is the initial parameter that has to be determined to set the surfactant feed rate. In any semicontinuous emulsion polymerization process, a convenient approach used to obtain the homogeneous composition of the resulting copolymer is to carry out the polymerization under monomer-starved conditions.[24] To determine the monomer feed rate that maintains the monomer-starved conditions, the maximum polymerization rate, R_p^{max}, in the monomer-starved regime needs to be known first.

For a conventional emulsion polymerization, the polymerization rate, R_p, during the growth stage is given in entirely general terms:

$$R_p = k_p \frac{\bar{n}}{N_A} [\mathrm{M}]_p N_p M_m \tag{19}$$

where k_p, $\bar{n}$, $[\mathrm{M}]_p$, and M_m are the propagation rate coefficient (cm^3/mol min), the average number of radicals per particle, the monomer concentration in the polymer particles (mol/L), and molecular weight of the monomer (or comonomer mixture; g/mol), respectively.

As pointed out by Wessling,[25] in monomer-starved, semicontinuous processes, R_m is considered roughly equal to R_p:

$$R_m \approx R_p \tag{20}$$

In a semicontinuous process, $[\mathrm{M}]_p$ can be expressed as follows:

$$[\mathrm{M}]_p = \frac{(W_{m0} + R_m t V_{a0})[1 - c(t)]}{\frac{1}{6}\pi D_v^3 N_p M_m} \tag{21}$$

Furthermore, the total volume of polymer particles could also be expressed in the following form:

$$\frac{1}{6}\pi D_v^3 N_p = \frac{(W_{m0} + R_m t V_{a0}) c(t)}{\rho} \tag{22}$$

It is assumed that the effect of monomer swelling on the volume of the polymer particles can be neglected.

With eqs. (21) and (22) combined, $c(t)$ can be expressed as follows:

$$c(t) = \frac{\rho}{[\mathrm{M}]_p M_m + \rho} \tag{23}$$

Rewriting eq. (23) gives the following:

$$[\mathrm{M}]_p = \frac{\rho}{M_m} \cdot \frac{1 - c(t)}{c(t)} \tag{24}$$

With eq. (24) substituted into eq. (19), R_p and $c(t)$ can be related simply by eq. (25):

$$R_p = k_p \rho N_p \frac{\bar{n}}{N_A} \cdot \frac{1 - c(t)}{c(t)} \tag{25}$$

For a copolymerizing system, k_p in eq. (25) is an average propagation rate coefficient, which can be determined from the composition of the comonomer mixture and the kinetic constants of the component comonomers. Schweer[26] developed an expression for k_p for kinetically controlled copolymerization, which is expressed as eq. (26):

$$k_p = \frac{r_1 m_1^2 + 2 m_1 m_2 + r_2 m_2^2}{\frac{r_1}{k_{11}} m_1 + \frac{r_2}{k_{22}} m_2} \tag{26}$$

where r_1 and r_2 are the reactive ratios of comonomers 1 and 2, m_1 and m_2 are the molar fractions of comonomers 1 and 2 in the comonomer mixture, and k_{11} and k_{22} are the rate coefficients for the homopropagation reactions of comonomers 1 and 2, respectively.

For BMA/BA copolymerization, ρ is 1.037 g/cm^3 for the 75 wt % BMA copolymer, as reported elsewhere,[10] and M_m for the 3:1 (w/w) BMA/BA comonomer mixture is 138.2 g/mol. Buback and Degener[27] reported that in the temperature range of 25–80°C, the rate coefficients for the homopropagation reaction of BA (comonomer 1) can be expressed as follows:

$$\log_{10} k_{\mathrm{BA}} = 6.0123 - 748.4/T \tag{27}$$

However, in the report of Hutchinson et al.,[28] from 10 to 90°C, the homopropagation rate coefficient for BMA (comonomer 2) can be written as follows:

$$\ln k_{\mathrm{BMA}} = (14.41 \pm 0.09) - (2472 \pm 29)/T \tag{28}$$

where T is the absolute temperature (K).

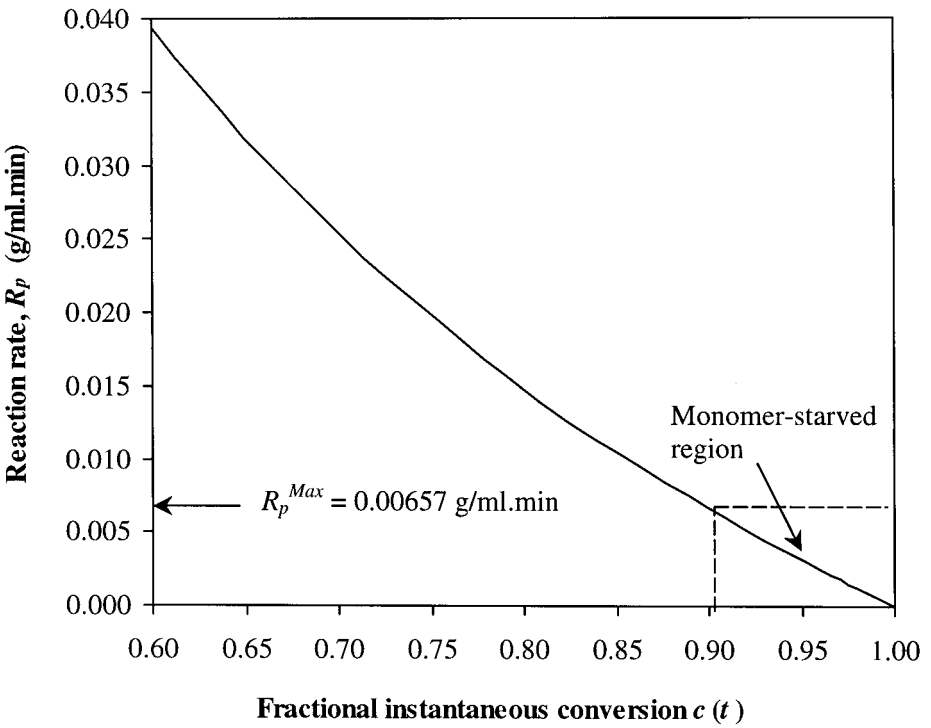

Figure 2 Relationship between R_p and $c(t)$ for an emulsion polymerization in a semicontinuous process. BMA/BA copolymerization (65/35 w/w) was used as an example ($N_p = 5.97 \times 10^{14}$ number/mL).

According to Paxton,[29] the reactivity ratios for BA and BMA at 50°C are 0.3 and 2.2, respectively. The molar fractions of BA and BMA in the comonomer mixture are $m_{BA} = 0.271$ and $m_{BMA} = 0.729$. After values of all these parameters were inserted into eq. (26), k_p was determined to be 1640.6 ± 276.7 L/mol s [(9.844 ± 1.660) $\times 10^7$ cm^3/mol min].

Figure 2 schematically illustrates the relationship of R_p and $c(t)$ described in eq. (25) for the BMA/BA copolymerization system.

Monomer-starved conditions are generally defined as the conditions under which the instantaneous conversion is greater than 90% [i.e., $c(t) \geq 0.9$].[24] Then, from eq. (25), the maximum value of R_p can be derived, only below which the monomer-starved conditions can be achieved. For different values of N_p, different values of R_p^{max}, only at or below which monomer-starved conditions can be reached, can be obtained by the selection of $c(t) = 0.90$ with eq. (25). The actual monomer feeding rate may be selected to be lower than or equal to R_p^{max} to maintain monomer-starved conditions.

Representative reaction kinetics

Figure 3 presents the kinetics of a typical semicontinuous emulsion polymerization reaction with the aforementioned methods to determine the surfactant and monomer feed rates. Figure 3(A) shows that with the monomer feed rate used (2.88×10^{-3} g/cm^3 min in this synthesis), which is lower than R_p^{max} (6.57×10^{-3} g/cm^3 min), the instantaneous conversions are higher than 90%, which means that the monomer-starved requirement is met. This should guarantee a homogeneous copolymer composition.[24] Experimental verification of the uniformity of the copolymer composition was also performed with DSC analysis by the scanning of the copolymer over a temperature range of −60 to 250°C. Only one obvious glass transition (around 0°C, i.e., the designed T_g) could be detected in the poly(BMA/BA) samples. This observation implies that a homogeneous composition of the resulting copolymer was achieved, even though further investigations are worthwhile. In addition, the particle number remained constant throughout the reaction, which resulted in monodispersity in the particle size distribution [Fig. 3(B)]. The characterization of these latex particles presented in Figure 3(B) shows that the number-average diameter (D_n) and weight-average diameter (D_w) are almost the same, and this indicates a narrow polydispersity index (PDI; D_w/D_n).

Independent control over the particle size and the concentration of carboxyl groups present on the latex particles

With the methods previously discussed for synthesizing noncarboxylated P(BMA/BA) copolymer latexes, the synthesis of well-defined carboxylated P(BMA/

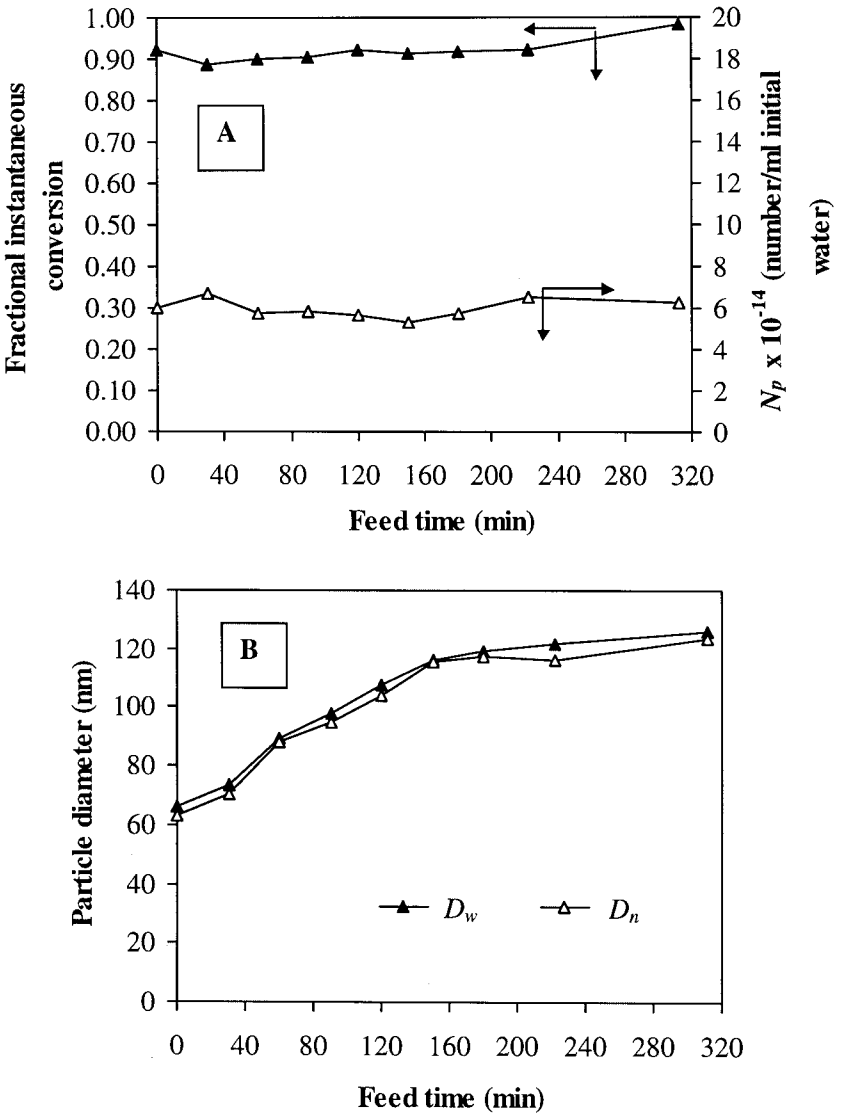

Figure 3 Sample synthesis of a P(BMA/BA) copolymer latex with a monomer-starved, semicontinuous emulsion polymerization process: (A) $c(t)$ and N_p as a function of the feed time and (B) the particle size as a function of the feed time (BMA/BA = 65/35 w/w; $N_p = 5.97 \times 10^{14}$ number/mL; $R_m = 2.88 \times 10^{-3}$ g/cm^3 min; $\alpha = 0.02$; $\beta = 0.87$; $W_{stot} = 0.20$ g; $D_{v0} = 65$ nm).

BA) latexes was greatly simplified. MAA was employed as the third comonomer for the incorporation of carboxyl groups into the latex particles. Similar calculations were used to choose the surfactant and monomer feed rates to obtain monodisperse carboxylated P(BMA/BA) latex particles with homogeneous copolymer compositions. Another parameter taken into consideration in this synthesis was the location of the carboxyl groups. This could be controlled by the time at which the MAA feed was started. In this example, we desired to obtain P(BMA/BA) copolymer latexes with carboxyl groups distributed throughout the particles. Therefore, the MAA feed was started at the same time at which the BMA and BA mixture was fed into the reactor. The process parameters and characterization results of the carboxylated P(BMA/BA) latexes synthesized by this method are listed in Table III.

As shown in Table III, monodisperse carboxylated P(BMA/BA) latexes were obtained. The surface carboxyl group coverage varied from 0 to 35% without any changes in the particle size or T_g of the latex copolymer. The distribution of the carboxyl groups was quite uniform as designed (the characterization is shown in a previous publication).[10] Independent control over the carboxyl group concentration was achieved by an adjustment in the ratio of BMA to BA. A question that may be raised here is how to adjust the ratio of BMA to BA so that the variation of the concentration of the carboxyl groups will not change T_g of the copolymer. This issue is discussed in the following section.

TABLE III
Parameters and Characterization Results for P(BMA/BA) Latexes Synthesized by Monomer-Starved, Semicontinuous Seeded Emulsion Polymerization

Parameter	Sample						
α	0.009	0.0005	0.009	0.0005	0.02	0.0005	0.009
β	0.255	0.255	0.255	0.255	0.870	0.255	0.255
W_{m0} (g)	35.0	35.0	35.0	35.0	7.0	35.0	35.0
V_{a0} (g)	450.0	450.0	450.0	450.0	90.0	450.0	450.0
W_{stot0} (g)	1.00	1.00	1.00	1.00	0.20	1.00	1.00
$R_m \times 10^4$ (g/ml min)	5.96	5.96	5.96	5.96	28.9	5.96	5.96
D_n (nm)	128.9	124.3	123.4	129.5	117.3	123.2	122.3
D_w (nm)	131.4	128.6	126.8	137.7	120.4	127.3	126.2
PDI (D_w/D_n)	1.019	1.035	1.028	1.063	1.026	1.033	1.033
MAA (wt %)[a]	0.00	0.86	0.88	2.68	2.90	5.65	5.98
σ_{COOH}[b]	0.00	6.75	7.29	14.20	14.70	33.34	35.90

D_{v0} = 65 nm; D_v predicted = 130 nm; weight percentage of PBMA in P(BMA/BA) was adjusted to obtain a T_g of approximately 0°C.

[a] Based on the polymer.

[b] Percentage of the particle surface area covered by carboxyl groups, taking 9 Å^2 as the cross-sectional area of each COOH group.[30]

Independent control over T_g and the concentration of carboxyl groups present on the latex particles

Because the carboxyl groups were incorporated by the copolymerization of MAA with BMA and BA and T_g of poly(methacrylic acid) (PMAA; 227.9°C[31]) was much higher than that of either poly(*n*-butyl methacrylate) (PBMA; 22.1°C, measured) or poly(*n*-butyl acrylate) (PBA; −54.2°C[31]), T_g of the carboxylated P(BMA/BA) copolymer increased with an increasing concentration of PMAA in P(BMA/BA) if the ratio of PBMA to PBA was not adjusted. In the monomer-starved, semicontinuous copolymerization process, the weight fractions of PBMA, PBA, and PMAA in the copolymer were equal to the weight fractions of BMA, BA, and MAA in the comonomer mixture, respectively. Because T_g of a random copolymer can be calculated with the equation of Pochan et al.[32] in combination with the conservation equation shown in eq. (30), the weight fractions of BMA (M_{BMA}) and BA (M_{BA}) can be plotted against the weight fraction of MAA (M_{MAA}) needed to keep T_g of the copolymer constant (e.g., at 0°C; Fig. 4). Therefore, the weight fractions of BMA and BA should be chosen according to Figure 4 for any weight fraction of MAA used to obtain the carboxylated P(BMA/BA) copolymer with a T_g value of 0°C:

$$T_g = M_{BMA}T_{g,BMA} + M_{BA}T_{g,BA} + M_{MAA}T_{g,MAA} \quad (29)$$

$$M_{BMA} + M_{BA} + M_{MAA} = 1 \quad (30)$$

The characterization of T_g's of the carboxylated P(BMA/BA) latexes with different concentrations of MAA (source of carboxyl groups) in the copolymer is shown in Figure 5. These results indicate that T_g's measured were near T_g's predicted by eq. (29). These results verify that independent control over T_g and the incorporation of carboxyl groups is feasible with the equation of Pochan et al. as a guide.

The described methods provide useful guidance for designing a semicontinuous emulsion polymerization process with the capability of determining the most important parameters, such as R_m, R_s, and the ratio of the comonomers for different reaction systems. This design provides an approach toward an overall control of the semicontinuous emulsion polymerization process for synthesizing well-defined, functionalized latex particles with independent control over the concentration of the functional groups (i.e., carboxyl groups), particle size, and T_g of the copolymer. As a summary of the aforementioned methods, a design flow chart is given in Figure 6.

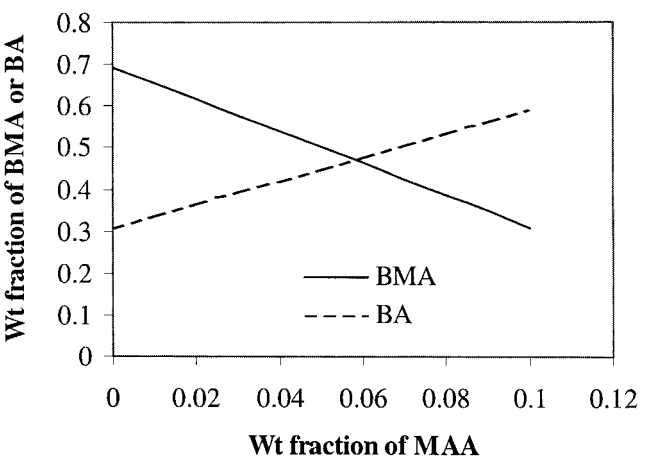

Figure 4 Weight fractions of BMA and BA as a function of the weight fraction of MAA for a constant T_g of 0°C for carboxylated P(BMA/BA) latex copolymers based on calculation with eqs. (29) and (30) ($T_{g,BMA}$ = 22.1°C; $T_{g,BA}$ = −54.2°C; $T_{g,MAA}$ = 227.9°C).

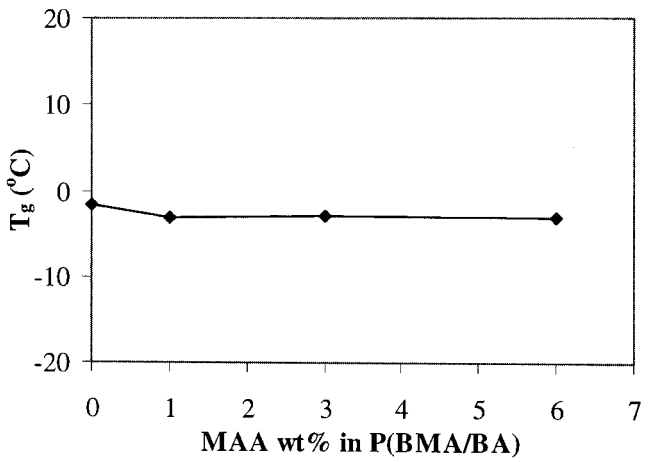

Figure 5 Measured T_g values of a carboxylated P(BMA/BA) copolymer as a function of the weight percentage of MAA (the source of carboxyl groups), with the weight fractions of BMA and BA chosen with eqs. (29) and (30). The calculated T_g was 0°C.

CONCLUSIONS

A simplified model has been developed to theoretically calculate the surfactant coverage on the latex particle surface and the maximum monomer feed rate that can be used to maintain monomer-starved conditions in a semicontinuous emulsion polymerization process. With this model, the surfactant coverage on the latex particles can be calculated at any given feed time, and it is known that the coverage changes as the feed time increases. The profile of the curve of the surfactant coverage versus the feed time is dependent on α. For a specific system, the particle number is kept constant when α is in a specific safe range. The model also derives a relationship between R_p and the instantaneous conversion, indicating a decrease in R_p when the instantaneous conversion increases. R_p^{max} can, therefore, be estimated with this calculation. Monomer-starved conditions can only be achieved at R_p's less than or equal to R_p^{max}. These calculations are very helpful in designing a semicontinuous emulsion polymerization process for synthesizing monodisperse latex particles with a homogeneous copolymer composition. They can also be extended to designing the synthesis of well-defined, functionalized latex particles, such as carboxylated latex particles. The concentration of carboxyl groups (from 0 to 36% in terms of surface carboxyl group coverage) in the carboxylated P(BMA/BA) latex particles can be adjusted independently of the particle size and T_g of the copolymers

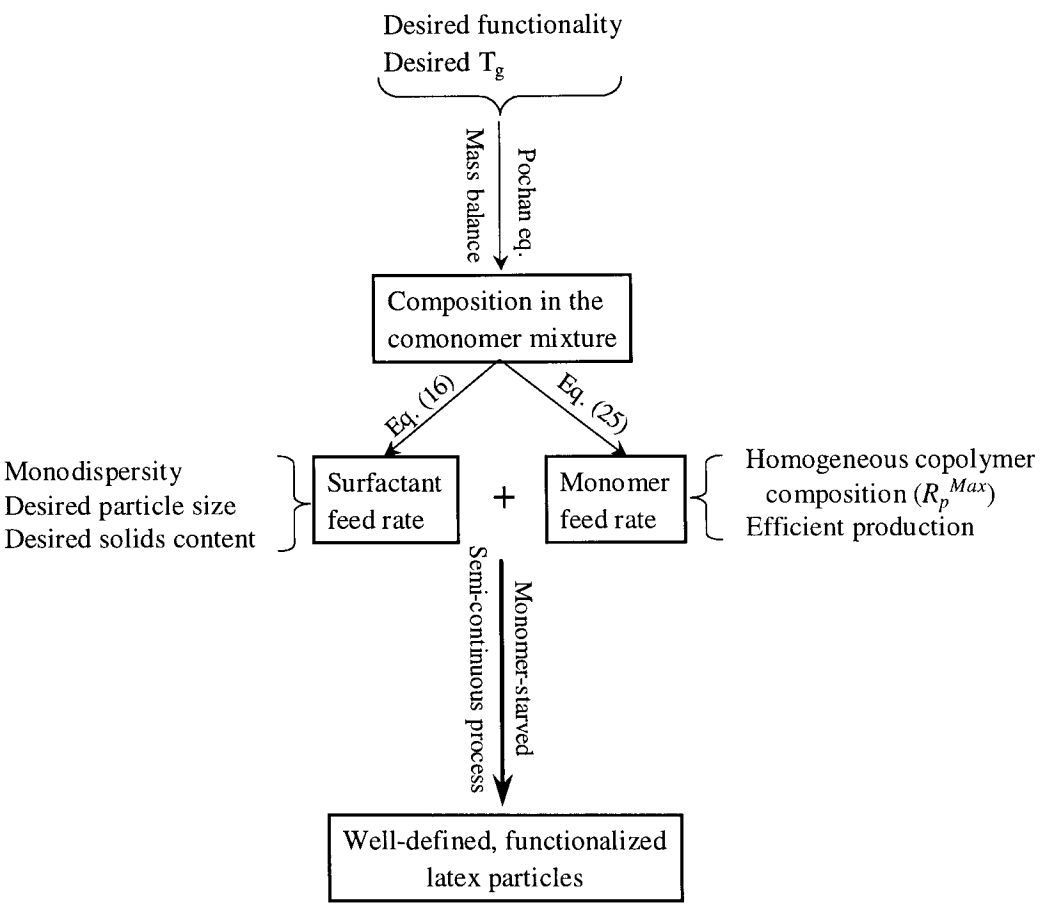

Figure 6 Schematic illustration of the monomer-starved, semicontinuous emulsion polymerization process design.

while a monodisperse particle size distribution and a homogeneous copolymer composition are maintained. T_g of the carboxylated P(BMA/BA) follows a linear equation (Pochan equation), which is used as the basis by which T_g can be adjusted with changes in the composition of the component comonomers.

NOMENCLATURE

a_s	latex particle surface area occupied by each surfactant molecule at the saturation surface surfactant coverage (cm^2)
cmc	critical micelle concentration of the surfactant (m*M*)
$c(t)$	fractional instantaneous conversion of the monomer or monomer mixture at feed time t
$c(t_0)$	fractional instantaneous conversion of the monomer or monomer mixture at the end of the seeding stage
d	distribution coefficient of the surfactant between the surfaces of the latex particles and the aqueous phase of the latex system
D_v	volume-average particle diameter (cm)
D_{v0}	volume-average particle diameter at the end of the seeding stage (cm)
k_{11} and k_{22}	rate coefficients for homopropagation reactions of comonomers 1 and 2, respectively
k_p	propagation rate coefficient (cm^3/mol min)
m_1 and m_2	molar fractions of comonomers 1 and 2, respectively
M_{BA}	weight fraction of the *n*-butyl acrylate structure unit in poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate)
M_{BMA}	weight fraction of the *n*-butyl methacrylate structure unit in poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate)
M_m	molecular weight of the monomer or comonomer mixture (g/mol)
M_{MAA}	weight fraction of the methacrylate acid structure unit in poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate)
$[M]_p$	monomer concentration in the polymer particles (mol/cm^3)
M_s	molecular weight of the surfactant (g/mol)
$\bar{n}$	average number of radicals per particle
N_A	Avogadro's constant (number/mol)
N_p	concentration of the latex particles at the end of the seeding stage in terms of the initial volume of the aqueous phase (number/cm^3)
N_{p0}	concentration of the latex particles in terms of the initial volume of the aqueous phase (number/cm^3)
r_1 and r_2	reactive ratios of comonomers 1 and 2, respectively
R_a	feed rate of deionized water in terms of the initial volume of the aqueous phase (g/min cm^3)
R_m	monomer feed rate in terms of the initial volume of the aqueous phase (g/min cm^3)
R_p	polymerization rate (g/min cm^3)
R_s	feed rate of the surfactant in terms of the initial volume of the aqueous phase (g/min cm^3)
$[S]_{aq}$	concentration of the surfactant present in the aqueous phase of a semicontinuous polymerization system (m*M*)
S_p	total surface area of the latex particles (cm^2)
t	feed time (min)
T	absolute temperature (K)
T_g	glass-transition temperature (K)
$T_{g,BA}$	glass-transition temperature of poly(*n*-butyl acrylate) (K)
$T_{g,BMA}$	glass-transition temperature of poly(*n*-butyl methacrylate) (K)
$T_{g,MAA}$	glass-transition temperature of poly(methacrylate acid) (K)
V_a	volume of the aqueous phase of the semicontinuous emulsion polymerization system at any feed time (cm^3)
V_{a0}	initial volume (before feeds) of the aqueous phase (cm^3)
W_m	weight of the monomer charged and fed into the semicontinuous polymerization system at any feed time (g)
W_{m0}	weight of the monomer used to prepare seeds (g)
W_{mf}	weight of the monomer fed (g)
W_s	total surfactant weight used to attain saturation coverage on the particle surface for the emulsion polymerization system, including the surfactant present on the particle surface and in the aqueous phase (g)
W_{sad}	weight of the surfactant adsorbed onto the surfaces of the latex particles (g)
W_{saq}	weight of the surfactant dissolved in the aqueous phase of the emulsion polymerization system (g)
W_{ssc}	weight of the surfactant needed to cover the entire surface of the latex particles in a monolayer coverage (g)
W_{stot}	total weight of the surfactant used in the semicontinuous emulsion polymerization system at a given feed time (g)
W_{stot0}	total weight of the surfactant used for the seeding stage in the semicontinuous emulsion polymerization system (g)
α	ratio of the surfactant feed rate to the monomer feed rate of the semicontinuous polymerization system
β	ratio of the water feed rate to the monomer feed rate of the semicontinuous polymerization system
ρ	density of the polymer or copolymer (g/cm^3)
σ_s	fractional surfactant coverage on the surfaces of the latex particles

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